

Lecture 7: Approximation Methods

Kit Matan

Mahidol University

In quantum mechanics, there are only a limited number of problems that can be solved exactly, most of which we have already considered in the previous lectures, for example a box potential, simple harmonic oscillator, hydrogen atom and etc. In general, there are two methods that we use to obtain exact solutions.

1. Diagonalization is used if a Hilbert space has a finite dimension, where a Hamiltonian operator can be represented by a matrix.
2. An operator method can be used for some of the problems with an infinite dimension Hilbert space, such as simple harmonic oscillator.
3. A differential equation method, in general, can be used to solve eigenvalue problems in an infinite dimension Hilbert space.

For most problems that cannot be solved exactly, there are several methods we can use to approximate solution to the eigenvalue problems.

1. Methods in solving differential equations
 - Shooting method
 - Finite difference method
2. Quantum Monte Carlo method
3. **Variational method** (you can skip this part)
4. **WKB (Wentzel-Kramers-Brillouin) method**

In this lecture, we will discuss the last two methods.

7.1 Variational method

For some problems that we cannot solve directly, we can guess an answer. A goal of the variational method is to solve for the ground state $|0\rangle$ and ground state energy E_0 of a Hamiltonian \mathcal{H} ,

$$\mathcal{H}|0\rangle = E_0|0\rangle.$$

We can guess a “trial ket” $|\tilde{0}\rangle$ that is “close” to the true ground state $|0\rangle$.

Theorem 7.1 Define

$$\bar{\mathcal{H}} \equiv \frac{\langle \tilde{0} | \mathcal{H} | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}$$

then

$$\bar{\mathcal{H}} \geq E_0,$$

for all “trial kets” $|\tilde{0}\rangle$.

We note that $|\tilde{0}\rangle$ might not be normalized.

Proof: Let $|n\rangle$ be eigenstates of \mathcal{H} , where $\mathcal{H}|n\rangle = E_n|n\rangle$.

$$\begin{aligned} \bar{\mathcal{H}} &= \frac{\langle \tilde{0} | \mathcal{H} | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle} = \frac{\sum_{n=0}^{\infty} \langle \tilde{0} | n \rangle E_n \langle n | \tilde{0} \rangle}{\sum_{m=0}^{\infty} \langle \tilde{0} | m \rangle \langle m | \tilde{0} \rangle} \\ &= \frac{\sum_{n=0}^{\infty} E_n |\langle n | \tilde{0} \rangle|^2}{\sum_{m=0}^{\infty} |\langle m | \tilde{0} \rangle|^2} \geq E_0 \frac{\sum_{n=0}^{\infty} |\langle n | \tilde{0} \rangle|^2}{\sum_{m=0}^{\infty} |\langle m | \tilde{0} \rangle|^2} \\ \Rightarrow \bar{\mathcal{H}} &\geq E_0, \end{aligned}$$

since $E_n \geq E_0$ for $n \geq 1$. ■

So, how can we use this theorem to systematically guess the ground state and ground state energy? The procedure below is a method of how to use the variational method to approximate the ground state energy.

1. Define a set of parameters which can be varied to minimize $\bar{\mathcal{H}}$. A trial ket is parameterized by these parameters,

$$\Rightarrow |\psi(\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n)\rangle$$

2. Calculate

$$\bar{\mathcal{H}}(\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n) = \frac{\langle \psi | \mathcal{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

3. Minimize $\bar{\mathcal{H}}$ by solving $\frac{\partial \bar{\mathcal{H}}}{\partial \lambda_i} = 0$, where $i = 1, 2, 3, \dots, n$.

For most cases, we can get a good approximation to E_0 with only a few parameters. We will discuss a few examples of how we can apply the variational method to estimate the ground state energy.

Example 1 Infinite-well one-dimensional potential where the potential energy is

$$V(x) = \begin{cases} 0 & -a \leq x \leq a \\ \infty & \text{otherwise} \end{cases}$$

In this case, we already know the exact solution for the ground state, which is

$$\psi_0(x) = \langle x | 0 \rangle = \frac{1}{\sqrt{a}} \cos\left(\frac{\pi x}{2a}\right)$$

and the ground state energy is

$$E_0 = \left(\frac{\hbar^2}{2m} \right) \left(\frac{\pi^2}{4a^2} \right).$$

However, suppose that we want to solve for $\psi_0(x)$ by guessing the ground state. We want to try a wave function which goes to zero at $x = \pm a$ and is maximum at the middle of the well. One of the functions that have these properties is a parabola

$$\tilde{\psi}_0(x) = a^2 - x^2.$$

$$\begin{aligned} \bar{\mathcal{H}} &= \frac{\left(\frac{-\hbar^2}{2m} \right) \int_{-a}^a (a^2 - x^2) \frac{d^2}{dx^2} (a^2 - x^2) dx}{\int_{-a}^a (a^2 - x^2)^2 dx} \\ &= \frac{10 \pi^2 \hbar^2}{\pi^2 8a^2 m} \\ \Rightarrow \bar{\mathcal{H}} &\simeq 1.0132 E_0. \end{aligned}$$

We can obtain a better approximation of the ground state by parameterizing the trial wave function,

$$\tilde{\psi}_0(x) = |a|^\lambda - |x|^\lambda,$$

where λ is the parameter that we will use to minimize $\bar{\mathcal{H}}$.

$$\Rightarrow \bar{\mathcal{H}} = \left(\frac{(\lambda + 1)(2\lambda + 1)}{2\lambda - 1} \right) \left(\frac{\hbar^2}{4ma^2} \right).$$

We then minimize $\bar{\mathcal{H}}$ with respect to λ by requiring that

$$\frac{\partial \bar{\mathcal{H}}}{\partial \lambda} = 0$$

We can solve for λ and $\bar{\mathcal{H}}_{min}$,

$$\lambda = \frac{1 + \sqrt{6}}{2} \simeq 1.72 \quad \text{and} \quad \bar{\mathcal{H}}_{min} = \left(\frac{5 + 2\sqrt{6}}{\pi^2} \right) E_0 \simeq 1.003 E_0,$$

which as you can see gives us a better approximation of the ground state energy than the unparameterized trial wave function. However, we will never get the true ground state wave function, which is a cosine function. This is one of the limitations of the variational method. That is, in general we cannot get the true ground state wave function from the trial wave function.

Next we can ask how well the trial wave function imitates the true ground state wave function. We assume that $|\tilde{0}\rangle$ is normalized and want to calculate the overlap between the trial state and the true ground state $\langle 0|\tilde{0}\rangle$.

$$\begin{aligned} \bar{\mathcal{H}}_{min} &= \sum_{n=0}^{\infty} |\langle n|\tilde{0}\rangle|^2 E_n \\ &= |\langle 0|\tilde{0}\rangle|^2 E_0 + \sum_{n=1}^{\infty} |\langle n|\tilde{0}\rangle|^2 E_n \\ &\geq |\langle 0|\tilde{0}\rangle|^2 E_0 + E_2 \left(\sum_{n=0}^{\infty} |\langle n|\tilde{0}\rangle|^2 - |\langle 0|\tilde{0}\rangle|^2 \right) \end{aligned}$$

We use E_2 instead of E_1 because $|1\rangle$ is odd and hence $\langle 1|\tilde{0}\rangle = 0$. The first non-zero contribution is $E_2 = 3^2 E_0$. Therefore, we have

$$\begin{aligned}\bar{\mathcal{H}}_{min} &\geq |\langle 0|\tilde{0}\rangle|^2 (E_0 - 9E_0) + 9E_0 \sum_{n=0}^{\infty} |\langle n|\tilde{0}\rangle|^2 \\ \Rightarrow |\langle 0|\tilde{0}\rangle|^2 &\geq \frac{9E_0 - \bar{\mathcal{H}}_{min}}{8E_0} = 0.99963 \equiv \cos \theta \\ \Rightarrow \theta &\leq 1.1^\circ,\end{aligned}$$

where θ denotes an “angle” between two vectors. This value is close to zero, which implies that the trial state $|\tilde{0}\rangle$ is close to the true ground state $|0\rangle$.

7.2 WKB method

Interpretation of wave function

We can think of the wave function in terms of “probability fluid”. We know that the probability density is

$$\rho(\vec{x}, t) = |\psi(\vec{x}, t)|^2,$$

where the probability of finding a particle in a one dimensional interval $a \leq x \leq b$ is

$$P(a \leq x \leq b) = \int_a^b |\psi(x')|^2 dx'$$

Consider $\frac{\partial \rho}{\partial t}$ for $\rho(\vec{x}, t)$ in three dimensions,

$$\Rightarrow \frac{\partial \rho}{\partial t} = \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t}.$$

From the Schrödinger equation, we know that

$$\begin{aligned}i\hbar \frac{\partial \psi}{\partial t} &= -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \\ \Rightarrow \frac{\partial \psi}{\partial t} &= \frac{i\hbar}{2m} \nabla^2 \psi - \frac{i}{\hbar} V\psi\end{aligned}$$

and for its complex conjugate, we have

$$\frac{\partial \psi^*}{\partial t} = \frac{-i\hbar}{2m} \nabla^2 \psi^* + \frac{i}{\hbar} V\psi^*.$$

Therefore,

$$\begin{aligned}\Rightarrow \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} &= \frac{-i\hbar}{2m} [-\psi^* \nabla^2 \psi + \psi \nabla^2 \psi^*] \\ &= \frac{-i\hbar}{2m} \nabla \cdot [\psi (\nabla \psi^*) - \psi^* (\nabla \psi)] \\ &= -\nabla \cdot \left[\frac{\hbar}{m} \Im(\psi^* \nabla \psi) \right].\end{aligned}$$

We define

$$\vec{j}(\vec{x}, t) = \frac{\hbar}{m} \Im(\psi^* \nabla \psi).$$

Then we obtain the continuity equation for the probability density, where $\vec{j}(\vec{x}, t)$ can be interpreted as “probability flux”.

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \vec{j}(\vec{x}, t),$$

or in an integral form

$$\frac{d}{dt} \int_V \rho dV = - \int_{\partial V} \vec{j} \cdot d\vec{A}.$$

\vec{j} is also related to momentum through

$$\int \vec{j} d^3\vec{x} = \Re \left[\frac{1}{m} \int \psi^* (-i\hbar \nabla) \psi d^3\vec{x} \right] = \frac{\langle P \rangle}{m}.$$

In the WKB approximation, we will write the wave function as

$$\psi(\vec{x}, t) = \sqrt{\rho(\vec{x}, t)} e^{\frac{i}{\hbar} S(\vec{x}, t)},$$

where $\sqrt{\rho(\vec{x}, t)}$ is an amplitude and $S(\vec{x}, t)$ is a phase, which can be related to the probability flux \vec{j} .

Physical significance of phase

We will discuss how the phase $S(\vec{x}, t)$ is related to the probability flux \vec{j} .

$$\begin{aligned} \psi^* \nabla \psi &= \sqrt{\rho(\vec{x}, t)} e^{-iS(\vec{x}, t)/\hbar} \left[\frac{1}{2} \frac{1}{\sqrt{\rho(\vec{x}, t)}} \nabla \rho + \sqrt{\rho(\vec{x}, t)} \frac{i \nabla S}{\hbar} \right] e^{iS(\vec{x}, t)/\hbar} \\ &= \frac{1}{2} \nabla \rho + \frac{i}{\hbar} \rho \nabla S \\ \Rightarrow \vec{j}(\vec{x}, t) &= \frac{\hbar}{m} \Im(\psi^* \nabla \psi) = \frac{\rho \nabla S}{m}. \end{aligned}$$

Therefore, the gradient of the phase ∇S determines the flow of the probability in the wave function. The faster the phase varies, the more the probability flux is.

Example 2 For a plane wave in one dimension,

$$\begin{aligned} \psi(x, t) &= e^{ipx/\hbar - iEt/\hbar} \\ \Rightarrow S(x, t) &= px - Et \\ \Rightarrow \nabla S &= \frac{dS}{dx} \hat{x} = \vec{p} = p_x \hat{x}. \end{aligned}$$

Therefore, $\frac{\nabla S}{m}$ can be thought of as a velocity \vec{v} , which implies that

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v}).$$

WKB Approximation

We will now start the discussion of the WKB approximation. From the Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi,$$

let

$$\psi(x, t) = e^{i\tilde{S}(x, t)/\hbar}.$$

Suppose that we can expand $\tilde{S}(x, t)$ in a power series of \hbar ,

$$\tilde{S} = S + S_1\hbar + S_2\hbar^2 + \dots.$$

Then we can rewrite ψ as

$$\psi = e^{\frac{i}{\hbar}(S + S_1\hbar + S_2\hbar^2 + \dots)} = \sqrt{\rho} e^{iS/\hbar},$$

where $\sqrt{\rho} = e^{\frac{i}{\hbar}(S_1\hbar + S_2\hbar^2 + \dots)}$. We do this expansion to make sure that S contains no \hbar term since later we will take S as a classical quantity. We substitute ψ back to the Schrödinger equation.

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} &= i\hbar \frac{\partial}{\partial t} \left(\sqrt{\rho} e^{iS/\hbar} \right) \\ &= i\hbar \left(\frac{\partial \sqrt{\rho}}{\partial t} + \frac{i}{\hbar} \sqrt{\rho} \frac{\partial S}{\partial t} \right) e^{iS/\hbar}, \end{aligned}$$

and

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi &= -\frac{\hbar^2}{2m} \nabla^2 \left(\sqrt{\rho} e^{iS/\hbar} \right) = -\frac{\hbar^2}{2m} \nabla \left[\left(\nabla \sqrt{\rho} + \frac{i}{\hbar} \sqrt{\rho} \nabla S \right) e^{iS/\hbar} \right] \\ &= -\frac{\hbar^2}{2m} \left[\nabla^2 \sqrt{\rho} + \frac{2i}{\hbar} \nabla \sqrt{\rho} \nabla S - \frac{1}{\hbar^2} \sqrt{\rho} (\nabla S)^2 + \frac{i}{\hbar} \sqrt{\rho} \nabla^2 S \right] e^{iS/\hbar}. \end{aligned}$$

Therefore, we have

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} &= -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \\ \Rightarrow i\hbar \left(\frac{\partial \sqrt{\rho}}{\partial t} + \frac{i}{\hbar} \sqrt{\rho} \frac{\partial S}{\partial t} \right) &= -\frac{\hbar^2}{2m} \left[\nabla^2 \sqrt{\rho} + \frac{2i}{\hbar} \nabla \sqrt{\rho} \nabla S - \frac{1}{\hbar^2} \sqrt{\rho} (\nabla S)^2 + \frac{i}{\hbar} \sqrt{\rho} \nabla^2 S \right] + \sqrt{\rho} V. \end{aligned} \quad (7.1)$$

We take a limit where $\hbar \rightarrow 0$,

$$\begin{aligned} \Rightarrow -\sqrt{\rho} \frac{\partial S}{\partial t} &= \frac{1}{2m} \sqrt{\rho} (\nabla S)^2 + \sqrt{\rho} V \\ \Rightarrow \frac{(\nabla S)^2}{2m} + V(x) + \frac{\partial S}{\partial t} &= 0, \end{aligned} \quad (7.2)$$

but $\nabla S = p$ and $\mathcal{H} = \frac{p^2}{2m} + V(x)$,

$$\Rightarrow \frac{\partial S}{\partial t} + H(x, \nabla S) = 0.$$

This equation is the classical equation of motion called ‘‘Hamilton-Jacobi equation’’. The partial differential equation Eq.?? can be used to solved for S .

Since we are interested in a stationary state, the solution can be written as

$$\psi(x, t) = \phi(x) e^{-iEt/\hbar},$$

where

$$\phi(x) \equiv \sqrt{\rho(x)} e^{iW(x)/\hbar}.$$

Therefore, we have

$$\rho = \rho(x) \quad \text{and} \quad S(x, t) = W(x) - Et,$$

and the Hamilton-Jacobi equation becomes

$$\frac{1}{2m} \left(\frac{\partial W}{\partial t} \right)^2 + V(x) - E = 0,$$

where $E = -\frac{\partial S}{\partial t}$, which is a constant of motion (energy), and $p = \frac{\partial S}{\partial x}$, which is a momentum. We can solve for $W(x)$,

$$\Rightarrow \boxed{W(x) = \pm \int_{x_0}^x dx' \sqrt{2m(E - V(x'))}} \equiv \int_{x_0}^x dx' p(x').$$

Now we consider the first order term in \hbar in Eq.??.

$$\begin{aligned} i\hbar \frac{\partial \sqrt{\rho}}{\partial t} &= -\frac{i\hbar}{m} \nabla \sqrt{\rho} \nabla S - \frac{i\hbar}{2m} \sqrt{\rho} \nabla^2 S \\ \Rightarrow \frac{\partial \rho}{\partial t} + \frac{1}{m} \nabla(\rho \nabla S) &= 0, \end{aligned}$$

which is the continuity equation since $\vec{j} = \frac{1}{m} \rho \nabla S$. For the stationary state, ρ is time-independent. Therefore,

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= 0 \\ \Rightarrow \rho \nabla S &= C', \end{aligned}$$

where C' is a constant. Since $\frac{\partial S}{\partial x} = p \propto v(x)$, where $v(x)$ is a velocity, we have

$$\Rightarrow \sqrt{\rho(x)} = \frac{C}{\sqrt{v(x)}},$$

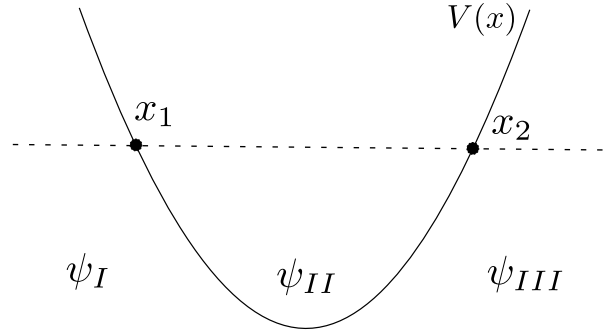
where C is a constant. Therefore, the final expression of the wave function in the WKB approximation is

$$\boxed{\psi(x, t) = \frac{C}{\sqrt{v(x)}} e^{\pm \frac{i}{\hbar} \left(\int_{x_0}^x p(x') dx' - Et \right)}$$

In the classical forbidden region where $V(x) > E$, we define $|p(x)| = \sqrt{2m(V(x) - E)}$ and $v(x) \rightarrow |v(x)|$. The wave function becomes

$$\boxed{\psi(x, t) = \frac{C}{\sqrt{v(x)}} e^{\pm \frac{1}{\hbar} \int_{x_0}^x \sqrt{2m(V(x') - E)} dx'}$$

In order to illustrate the application of the WKB approximation, we will consider the following potential.



The amplitude of the wave function diverges at x_1 and x_2 because $\frac{1}{\sqrt{v(x)}} \propto \frac{1}{(E - V(x))^{1/4}}$ and $E = V(x)$ at x_1 and x_2 . If we consider the wave function from the left of x_1 through x_1 from ψ_I to ψ_{II} , we find that

$$\psi_I(x) = \frac{1}{(V - E)^{1/4}} e^{\frac{1}{\hbar} \int_{x_1}^x dx' \sqrt{2m(V(x') - E)}} \rightarrow \psi_{II}(x) = \frac{2}{(E - V)^{1/4}} \cos\left(\frac{1}{\hbar} \int_{x_1}^x dx' \sqrt{2m(E - V(x'))} - \frac{\pi}{4}\right),$$

where the phase shift of $\frac{\pi}{4}$ is due to the asymptotic behavior of the Airy function. Similarly, the wave function from the right of x_2 through x_2 from ψ_{III} to ψ_{II} can be described by

$$\psi_{III}(x) = \frac{1}{(V - E)^{1/4}} e^{-\frac{1}{\hbar} \int_{x_2}^x dx' \sqrt{2m(V(x') - E)}} \rightarrow \psi_{II}(x) = \frac{2}{(E - V)^{1/4}} \cos\left(\frac{1}{\hbar} \int_{x_2}^x dx' \sqrt{2m(E - V(x'))} + \frac{\pi}{4}\right)$$

However, in Region *II*, the phase difference between ψ_{II} from the left and from the right must be $n\pi$, where n is an integer. In other words, the two functions on the right hand side must be equal up to a minus sign. Since physically we can only measure $|\psi|^2$, the difference of a minus sign yield the same result. And we note that

$$\pm \cos \theta_1 = \cos \theta_2 \Rightarrow \cos(n\pi + \theta_1) = \cos(\theta_2) \Rightarrow \theta_2 - \theta_1 = n\pi.$$

Therefore, we must have

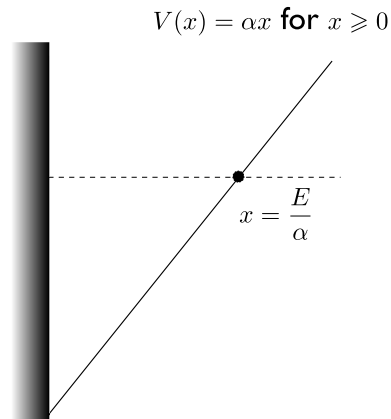
$$\Rightarrow \frac{1}{\hbar} \left[\int_{x_1}^x dx' \sqrt{2m(E - V(x'))} + \int_x^{x_2} dx' \sqrt{2m(E - V(x'))} \right] - \frac{\pi}{2} = n\pi,$$

which implies that

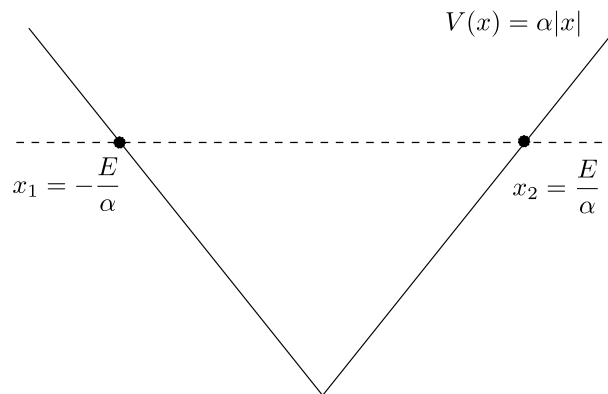
$$\boxed{\int_{x_1}^{x_2} dx' \sqrt{2m(E - V(x'))} = \left(n + \frac{1}{2}\right) \pi \hbar}$$

This equation is known as the *Bohr-Sommerfeld quantization*, which gives rise to the quantization of energy. We note that the Bohr-Sommerfeld quantization gives a good approximation (reliable result) when the change of momentum in one wavelength is very small. In other words, the quantity inside the integral changes slowly as a function of x .

Example 3 Consider a particle in a potential depicted in the figure below.



where $\alpha > 0$. The WKB approximation will not work very well for this potential especially at $x = 0$ because the change of momentum at the wall is very rapid. Therefore, we will modify the above potential and consider the second potential shown in the figure below instead.



We can see that for $x \geq 0$ the two potentials are the same. The advantage of using the potential in the second figure is that the change of momentum at $x = 0$ becomes smoother and hence the WKB approximation will yield a better result (closer to the true eigenenergies). Then, by realizing that for the first potential the wavefunction must vanish at $x = 0$, we only need to choose the odd wavefunction, which means odd integers, from the solutions for the second potential.

The quantization of energy of the second potential is given by

$$\begin{aligned}
 \int_{x_1}^{x_2} dx' \sqrt{2m(E - V(x'))} &= \int_{-E/\alpha}^{E/\alpha} dx' \sqrt{2m(E - \alpha x')} \\
 &= 2 \int_0^{E/\alpha} dx' \sqrt{2m(E - \alpha x')} = 2 \int_0^{E/\alpha} dx' \sqrt{2mE} \left(1 - \frac{\alpha x'}{E}\right)^{1/2} \\
 &= 2E^{3/2} \left(\frac{\sqrt{2m}}{\alpha} \int_0^1 dy (1-y)^{1/2} \right) \quad \text{where } y = \frac{\alpha}{E} x' \\
 \Rightarrow 2\gamma E_n^{3/2} &= \left(n + \frac{1}{2}\right) \pi \hbar, \tag{7.3}
 \end{aligned}$$

where $\gamma = \frac{\sqrt{2m}}{\alpha} \int_0^1 dy (1-y)^{1/2}$, which is a constant. This result is for the quantization of energy of the second potential. We can use this solution to approximate the energy of the first potential by realizing that only odd n can exist. That is

$$n \rightarrow 2n' + 1$$

Therefore, we have

$$\begin{aligned} 2 \int_0^{E/\alpha} dx' \sqrt{2m(E - \alpha x')} &= \left(2n' + 1 + \frac{1}{2}\right) \pi \hbar \\ 2\gamma E_{n'}^{3/2} &= \left(2n' + \frac{3}{2}\right) \pi \hbar \\ \Rightarrow \gamma E_{n'}^{3/2} &= \left(n' + \frac{3}{4}\right) \pi \hbar, \end{aligned}$$

where $n' = 0, 1, 2, \dots$.